Multilayer synthetic object

Field of the invention

The present invention relates to a method for realizing multilayer objects by compression molding of a multilayer dose.

Prior art

Patent US 4 876 052 describes a multilayer object (figure 1), characterized in that a first synthetic resin 3 is fully imprisoned inside a second synthetic resin 2. This multilayer object is obtained by compression molding of a composite dose in which the first resin is totally imprisoned in the second resin. The multilayer structure described in patent US 4 876 052 is particularly interesting for objects such as receptacles or lids. However, the objects obtained according to the method described in patent US 4 876 052 require a large proportion of functional resin in the object, thereby engendering two major drawbacks: the first being a prohibitive cost and the second a lowered resistance to mechanical stresses. The lack of adhesion between the functional resin and the outer resin reduces the solidity of the object and creates a risk of decohesion of the outer layer. Another drawback of patent US 4 876 052 lies in the fact that the respective quantity of the resins 2 and 3 is only poorly adjustable. As will be shown further below in the account of the invention, these quantities are fixed by the geometry of the object and by the flows during the compression of the dose. This method likewise calls for the intermittent extrusion of the first resin inside a second resin. Patent US 4 876 052 describes a coextrusion device having a shut-off valve mechanism for the first synthetic resin.

To eliminate the drawbacks of patent US 4 876 052, Japanese patent JP 2098415 proposes the realization of

a multilayer object by compression molding starting from a composite dose, characterized in that the *second* synthetic resin covers only the side faces of the first synthetic resin. The compression molding of this dose along its axis of symmetry produces an object having a multilayer structure (figure 2), characterized in that a first resin 2 partially imprisons a second resin 3. However, the multilayer objects realized from two resins according to patent JP 2098415 have two major drawbacks: the first being that of having the barrier resin 3 exposed on a central surface area of the object over at least 10% of the total surface area of the object, and the second being that of requiring a quantity of barrier resin 7 in the object amounting to at least 30% of the total quantity of resin. This produces, on the one hand, objects having a prohibitive cost and, on the other hand, objects having heavily modified mechanical properties, mainly in the center of the object. Another drawback of patent JP 2098415 lies in the fact that the respective quantity of the resins 2 and 3 is only slightly adjustable, these quantities being fixed by the geometry of the object and by the flows during the compression of the dose.

In patent JP 2098415, it is proposed to use a triple-layer dose in order partially to eliminate the aforesaid drawbacks. This dose is constituted by a first resin 4 forming the central part of the dose, by a second resin 3 covering only the side faces of the first resin, and by a third resin 2 covering only the side faces of the second resin. The crushing of this composite dose along its axis of symmetry produces a multilayer object (figure 3). The use of a triple-layer dose has the advantage of reducing the quantity of functional resin 3 used and produces objects having slightly modified mechanical properties in relation to the same object containing a single resin 2. However, the second resin 3 does not cover the central part of the multilayer object, which produces multilayer

objects without barrier property close to the axis of symmetry. This central region of the object not covered by the barrier resin layer 3 weakens the barrier performance of the object and renders this solution less effective.

Patent application CH01619/04 describes multilayer objects (figure 4) realized from a compression-molded multilayer dose. The objects described in this patent application have a multilayer structure characterized by the position of the functional layer forming a zigzag-shaped double fold. The functional layer is distributed correctly throughout the object, even in the central part. The method for realizing multilayer objects which is described in patent application CH01619/04 also allows control of the thickness of the functional layer. An adhesive layer can be added between the resin forming the surface of the object and the functional resin. However, the compression of the dose calls for a method and a specific molding device. This method calls especially for additional die tool movements relative to the basic compression process, setting the two parts of the mold in relative motion. In the case of high-speed molding, it can be detrimental to use a compression device as described in patent application CH01619/04.

Patent EP926078 describes the obtention of a plug liner (figure 5) by compression molding of a dose containing a laminar multilayer structure. The functional resin 3 forms strips dispersed in the resin 2. The method consists in extruding a laminar dose (millefeuille sort) with a strip-generating device, then in compressing the dose so as to form the liner. In the thickness of the liner (figure 5), a multilayer structure of the millefeuille type is found. This method consists in compression-molding a laminar alloy, the number of strips in the dose being very large in number. This method has the drawback of requiring a

high barrier resin percentage (in the order of 20%) in order significantly to reduce the permeability of the object, since the strips do not form a continuous layer. Another drawback of patent EP926078 lies in the fact that the position of the strips in the object cannot be controlled. The result is that the resin forming the surface layer of the multilayer object is a mixture of different dose-forming layers. This can limit the use of the objects described in patent EP926078, for hygiene reasons, when the packaged product is in contact with the laminar multilayer object. Another drawback of patent EP926078 is linked to the limited choice of resins, which must exhibit viscosities and melting temperatures which allow the strips to be maintained during the compression of the dose.

Subject of the invention

The invention relates to the realization of multilayer objects realized by compression molding of a multilayer dose, while allowing the elimination of the aforesaid drawbacks.

Summary of the invention

The invention consists in an axisymmetrical multilayer object forming a wall of thickness E, said object being composed of a first resin forming the structure of the object and representing at least 80% of the volume of the object, and of a second resin forming at least two fine functional layers, said functional layers being imprisoned separately in the first resin, the multilayer structure being characterized in that

a. the functional layers are distributed in separate parts of the object
b. the functional layers form bodies of revolution centered on the axis of symmetry of the object

c. the two functional layers are placed partially one on top of the other in a direction perpendicular to said wall.

Detailed description of the invention

A better understanding of the invention will be gained below from a detailed description of the examples illustrated by the following figures.

Brief description of the figures

Figures 1 to 5 illustrate multilayer objects of the prior art.

Figure 1 shows a multilayer object described in patent US4876052. This object 1, realized by compression molding, comprises a functional resin layer 3 fully encapsulated in a resin 2 forming the visible surface of the object.

Figure 2 illustrates a multilayer object described in patent JP2098415. This object 1 comprises a functional resin layer 3 partially encapsulated in a resin layer 2 forming the visible surface of the object.

Figure 3 shows another multilayer object described in patent JP2098415. This object comprises a fine layer of functional resin 3 imprisoned between two layers of resins 2 and 4 forming the object.

Figure 4 shows a multilayer object described in application CH01619/04. This object is characterized by the zigzag-shaped double fold of the functional layer 3.

Figure 5 shows an object comprising a laminar multilayer structure described in patent EP926078.

Figures 6 to 11 show multilayer objects corresponding to the invention.

Figure 6 illustrates a first multilayer object conforming to the inventive concept. The multilayer structure is observed in a sectional plane passing through the axis of symmetry of the object. The functional layers 3, 5 and 7 form an overlap.

Figure 7 shows a second example of a multilayer object having a central surface area S not covered by the functional layers.

Figures 8 and 9 illustrate objects realized according to the invention and having an orifice 15.

Figure 10 shows a multilayer plug realized according to the invention.

Figure 11 shows a multilayer preform realized according to the invention.

Figure 12 illustrates the flow profile during the compression of the dose.

Figure 13 shows the method for obtaining multilayer objects and, in particular, the relationship between the dose and the object.

Figure 14 shows how the ratio S/Sp, of the surface area not covered by the functional layer over the surface area of the object, varies as a function of the compression rate H/E.

Figure 15 illustrates the realization of an object according to patent JP 20418415.

Figure 16 shows how the ratio S/Sp varies as a function of H/E for an object realized according to patent JP 20418415.

Figure 17 shows another example of the realization of an object according to the invention.

Detailed description of the figures

The invention relates to a multilayer object possessing at least two independent layers of functional resin distributed in fine layer in a second resin forming the structure of the object, said layers being distributed in separate parts of the object and forming a partial overlap. The term "functional resin" designates a resin chosen for its barrier properties with respect to gases or to aromas.

Figure 6 illustrates a multilayer object corresponding to the invention. The thickness of the object is observed along a section realized perpendicular to the surface of the object and passing through the axis of symmetry. This figure shows the distribution of the functional layers in the thickness of the part. The functional resin forms the fine layers 3, 5 and 7 distributed in the base resin forming the structural layers 2, 4 and 6 of the object. The quantity of functional resin represents generally less than 10% of the total resin volume. In order to obtain advantageous barrier properties, it was observed that the functional layers had to be placed partially one on top of the other so as to form the overlap L. In a preferred embodiment (not illustrated), a value of the overlap L ranging between 1 and 3 times the thickness E allows a permeability to be obtained which is close to that obtained with a single continuous layer of identical thickness. In figure 6, the central part of the object is formed by the layer 7 of functional resin. The quantity of functional resin forming the central layer

7 of the object represents less than 5% of the total resin volume and generally less than 3%. The central layer 7 of functional resin is present over a surface area S representing less than 3% of the total surface area of the object, and preferably less than 1%. The ends 9, 10 and 11 of the functional resin layers 3, 5 and 7 are situated proximate to the top and bottom surfaces of the object, the ends of which aforementioned layers can lie flush with the surface of the object or be totally encapsulated. The functional layers 3, 5 and 7 form, respectively, the folds 12, 13 and 14. The fold 12 of the layer 3 is generally situated proximate to the side wall of the object so as to have impermeability properties over the whole of the surface of the object. In certain cases, it is not necessary to make the whole of the surface of the object impermeable, in which case the invention allows said layer 3 to be spread solely in the part in which the object must be impermeable. The folds 13 and 14 of the functional resin layers 5 and 7 are placed one on top of the other at the ends 9 and 10 of the functional layers 3 and 5 and form an overlap. The overlap of the functional layers allows a good level of impermeability to be assured, despite the discontinuity created by the different layers.

Figure 7 shows a second example of a multilayer object realized according to the invention, this object being distinguished from the object presented in figure 6 by its central part. The object presented in figure 7 shows the arrangement of the independent functional layers 3, 5 and 7 in the resin layers 2, 4, 6 and 8 forming the structure of the object. The functional resin layers 3, 5 and 7 form the respective folds 12, 13 and 14. The folds 13 and 14 are placed one on top of the other at the ends 9 and 10 of the functional resin layers 3 and 5 and form an overlap by which a good level of impermeability can be assured. The ends 11 of the functional resin layer 7 do not cover the central

part of the object, leaving a permeable surface area S. The leak created by the surface area S was found to be very small, considering the ratio S/Sp of the surface area not covered by the functional layers over the total exposed surface area. The invention allows a ratio S/Sp of less than 2% to be obtained, which produces negligible leaks.

Figure 8 illustrates a third multilayer object realized according to the inventive method. This object 1 contains a central orifice 15, as well as two fine layers 3 and 5 of functional resin distributed between the layers 2, 4 and 6 of the resin forming the structure of the object. The functional layers 3 and 5 form folds 12 and 13, the fold 13 being superposed with the ends 9 of the functional layer 3.

Figure 9 shows another example of a multilayer object, having an orifice. This object differs from the object presented in figure 8 by the orientation of the folds 12 and 13 of the functional resin layers 3 and 5.

The method for realizing multilayer objects which is set out below is particularly advantageous for realizing objects such as plugs, lids, preforms, or, indeed, tube shoulders. This method can likewise advantageously be used to realize preforms in the form of a slab, which slabs are then used in thermoforming or blow thermoforming to form multilayer objects. Figure 10 illustrates a multilayer structure which might be obtained in a geometry of a plug-type object and figure 11 shows a multilayer preform realized according to the invention. These objects have a partial superposition of the functional resin layers, by which the impermeability of the object can be assured.

Figure 10 shows that the functional layer 3 is generally the combination of three fine parallel layers

3a, 3b, 3c, the layers 3b and 3c being adhesive layers situated on either side of the barrier layer 3a. This combination allows resins of different nature to be combined, while assuring good adhesion between the different layers, which prevents possible problems of delamination or decohesion in the multilayer objects. The adhesive and barrier layers lie parallel and are small in quantity. The aggregate of the adhesive layers 3b and 3c and of the barrier layer 3a forming the functional layer 3 generally represents a quantity of resin less than 15% of the total resin volume forming the dose, and preferably a quantity interior to 10%.

The method for realizing multilayer objects according to the invention is particularly advantageous, for it requires very little modification of the existing devices. As will be show further below, this method allows multilayer objects to be realized at high production speed.

The method consists in coextruding a cylindrical or tubular multilayer dose, in feeding this multilayer dose in the molten state into a compression device, then in compressing said dose in a mold so as to form the object, this method being characterized by the geometry of the multilayer dose (height, diameter) and the position of the functional layers in said dose.

In order to gain a better understanding of the spirit of the invention, it is necessary to grasp the link connecting the multilayer dose to the multilayer object. Figure 12 shows the flow of the resins during the compression of the dose. This flow is mainly dependent on the rheological properties of the resins during the compression, as well as on the geometry of the object. Figure 12 shows that this flow is faster midway between the walls than close to the walls of the die tool. Proximate to the walls of the die tool, the displacement velocity of the particles tends toward

zero, but the shear deformation is high. Conversely, midway between the walls, the velocity of the particles is at a maximum and the shear deformation is at a minimum. During the flow, the functional resin layer is entrained and deformed in a non-uniform manner according to its position in the flow profile. The final position of the functional resin layer in the object is thus determined by the original position of the functional layer in the dose and by the sum of the deformations suffered during the flow.

Figure 13 shows the multilayer dose 16 used to realize a multilayer object 1. A cylindrical dose 16 corresponding to a portion of coextruded multilayer rod comprises two fine layers 3 and 5 of functional resin imprisoned between the layers 2, 4 and 6 of the base resin. The dose 16 corresponds to a radial stacking of tubular layers, the central layer 6 being cylindrical. The proportion of functional resin does not generally exceed 20% of the volume of the dose, and this quantity is generally less than 10%. The compression of this dose generates a flow of resin toward the periphery, which entrains and deforms the functional layers 3 and 5 in this direction. The obtained multilayer object 1 is illustrated in figure 13. In this object can be found the functional resin layers 3 and 5 forming a fold in the direction of the flow, the fold 13 of the functional layer 5 forming an overlap L with the end 9 of the functional layer 3. The value of the overlap L and the spread of the fold 12 out to the end of the object are linked to the original geometry of the dose and to the position of the functional layers in the dose. To obtain a multilayer object as illustrated in figure 13, it is necessary to position the resin layers 3 and 5 correctly in the dose. The geometry of the dose and the position of the functional layers in the dose can be defined by calculation or experimentally. It is observed experimentally that the ratio of the radial positions Ri and Rj of two adjacent functional layers i

and j is constant and less than or equal to 0.5, the layer i being situated closer to the axis of symmetry than the layer j.

The object 1 illustrated in figure 13 has a central surface area S not covered by the functional layer. The ratio S/Sp, corresponding to the ratio to the non-covered surface area over the surface area of the object, is presented in figure 14. This ratio has been found to depend on the compression rate of the dose, that is to say on the ratio H1/E, H1 corresponding to the height of the dose and E to the thickness of the object. Figure 14 shows how the ratio S/Sp varies as a function of H1/E. It is observed experimentally that for compression rates of 5, the ratio S/Sp of the object 1 was less than 10%, and for a compression rate of 10, this ratio was less than 2%. This result indicates that for a compression rate of 10, the leak-engendering surface area S represents less than 2% of the surface area of the object.

In order to show the advantage of objects realized according to our invention, these have been compared to objects obtained according to the method described in patent JP 2098415.

Figure 15 illustrates the compression of a dose such as proposed in patent JP 2098415 so as to demonstrate the limits of the multilayer objects obtained according to this method and better understand the object of the present invention. Figure 15 shows a triple-layer dose 16 realized according to patent JP 2098415. This dose contains a first resin 4 forming the central part of the dose, a functional resin 3 covering only the side faces of the first resin, and a third resin 2 covering only the side faces of the functional resin. Figure 15 illustrates the object 1 obtained following compression of the dose 16. The functional layer 3 has spread out to the end of the object, while remaining encapsulated

at the level of the periphery of the object. As figure 15 shows, the functional layer has not spread into the central part of the object 1.

The experimental findings corresponding to the realization of multilayer objects according to patent JP 2098415 have been plotted in figure 16. This figure shows how the fraction of surface area not covered by the functional layer S/Sp varies as a function of the compression rate H/H1. It is observed experimentally that for compression rates of 5 the ratio S/Sp of the object 1 is greater than 25%, and for a compression rate of 10 this ratio close to 20%. This finding indicates that for a compression rate of 10, the leak-engendering surface area S represents approximately 20% of the surface area of the object.

The barrier properties of objects realized according to patent JP 2098415 (figure 15) and according to the invention (figure 13) have been compared. Disks of 1 mm thickness and of 40 mm diameter have been realized starting from cylindrical multilayer doses of height H1 close to 10 mm and of diameter substantially equal to 12.7 mm. The base resin used is an HDPE (high-density polyethylene), the functional resin used is an EVOH (ethylene vinyl alcohol). The measure of oxygen permeability shows that objects realized according to the invention are approximately 5 to 10 times more barrier-forming than objects realized according to patent JP 2098415. In both cases, 8% of functional resin was used. The overlap L of the functional layers measures approximately 1 mm.

Figure 17 illustrates a second example of the realization of multilayer objects. A dose 16 comprising functional resin layers 3, 5 and 7 encapsulated laterally in the resin layers 2, 4 and 6. The functional resin layer 7 forms the central part of the dose. This dose is realized from a rod which has been

coextruded and periodically cut as it leaves the coextrusion head. This dose is next transferred into a compression mold, then compressed. The vertical compression of the dose 16 along its axis of symmetry produces the object 1 represented in figure 17. The functional resin layer 7 renders the central part of the object impermeable.

The method for realizing multilayer objects according to the invention calls for the realization of multilayer doses. A first method consists in coextruding a multilayer rod or tube at constant flow rate and in periodically cutting the rod or tube, as it leaves the die tool, in order to form the doses. This first method can be advantageous for making multilayer objects at high speed. A second method consists in forming the doses by virtue of a discontinuous periodic flow, the quantity of material coextruded over a period forming a dose. This second method can be advantageous for obtaining multilayer doses having great regularity in terms of weight.

The cutting of the dose can be realized according to known methods. In this connection can be cited, for example, rotary cutters for cutting the rod as at leaves the extruder. This type of cutter can simultaneously be used to transfer the dose into the mold. A dose-cutting method by shutting off the extrusion duct is used in discontinuous extrusion devices.

The transfer of the dose can be effected by known methods, such as by gravity or by means of a transfer device. The positioning of the dose in the compression mold must be precise and, in particular, the axis of symmetry of the dose must be precisely aligned with the axis of symmetry of the cavity of the mold. The doses are compressed along the axis of symmetry of the dose.

The multilayer doses are extruded in the molten state at temperatures suited to the resins used. The multilayer doses remain in the molten state during the step of being transferred into the compression mold. The doses are compression molded and the object obtained is at least partially cooled in the mold prior to ejection.

The resins used within the scope of the invention correspond to the thermoplastic resins currently being used, and more particularly to those used in the packaging industry. Amongst the barrier resins which may be used to form the functional layers 3, 5 and 7 can be cited ethylene vinyl alcohol copolymers (EVOH), polyamides such as Nylon-MXD6, acrylonitrile-methyl acrylate copolymers (BAREX), fluorinated polymers such as PVDF. In this connection can also be cited a few resins which may be used for the layers 2 and 4, 6 and 8 forming the structure of the object: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide (PA), polyester (PET). This list is not exhaustive. In the choice of resins, it is important to select products which have neighboring viscosities. In general, it is preferable to use resins which, at working temperature, have a viscosity ratio less than 10, and preferably a viscosity ratio less than 3 will be chosen.

The devices used in the realization of objects according to the invention are known. The device minimally comprises means for coextruding multilayer doses, means for transferring the multilayer dose into a compression mold, and means for compressing the dose so as to form the object.

The invention has the advantage of allowing the production of multilayer objects at high production speed without substantial modifications relative to a device used in the realization of single-layer objects.

The invention calls for the replacement, in particular, of the single-layer extrusion device by a multilayer extrusion device.

In the examples which are presented here, the doses and the objects are of simple geometry, but the invention obviously relates to any geometry of dose and of object.

The objects obtained according to the invention contain at least two functional layers, each forming a fold and placed partially one on top of the other. The invention also allows objects to be obtained which contain a plurality of functional layers placed one on top of the other, each of which is able to form more than one fold. Zigzag-shaped functional layers are obtainable.

Numerous arrangements of the functional layers in the dose are possible. It may be advantageous to couple to the invention a particular arrangement of the functional layers, said arrangement being characterized in that the functional layers have a variable distance to the axis of symmetry. According to this variant, at least one functional layer forms the shell of a body of revolution centered on the axis of symmetry, and the distance of said layer to the axis of symmetry is variable.

Other dose geometries may be used. It has been observed that doses which have a part of their surface concave are particularly advantageous. Such dose geometries facilitate good distribution of the functional layers in the multilayer object.

The realization of packagings or packaging components for food applications calls for good hygiene properties. It is thus often desirable for the functional layers not to be in direct contact with the packaged product. It may be advantageous to imprison

the functional layers totally in the dose, such that said functional layers are totally imprisoned in the object.

Alternatively, it is possible for just one end of the barrier layer not to be imprisoned.